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I, JONNE YABSLEY, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2002953099 for a patent by AUSTRALIAN COMPOSITES PTY LTD as filed on 04 December 2002.



WITNESS my hand this
Nineteenth day of December 2003

JONNE YABSLEY
TEAM LEADER EXAMINATION
SUPPORT AND SALES

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PROVISIONAL SPECIFICATION

Invention Title: **Reinforced Polymer Composition**

The invention is described in the following statement:

REINFORCED POLYMER COMPOSITION

The present invention relates to a cross-linkable polymeric fibre coating composition and method of preparing same. The invention also relates to articles formed using this process.

5 Continuous fibre reinforced polymer matrix materials (hereinafter referred to as "reinforced polymer materials") are used for numerous flat and curved panel applications in the aerospace/aeromotive, industrial, chemical, building and sporting goods industries.

Traditionally, reinforced polymer materials are manufactured by the "lay-up" method. Fibres are laid over the mould and the polymer resin is poured and worked into the fibres, and cured *in situ*. The two most common and serious material defects in reinforced polymer materials are (i) poor wetting of the fibre by the resin with appearance of voids in the polymer matrix, and (ii) excessive wetting of the fibre with resin rich pocket creation. Both of these defects can prevent the material from reaching its maximum potential in mechanical properties and can cause premature failure of the material when in use. The lay-up method is unsuitable for achieving maximum mechanical properties in a consistent and reliable manner.

Partially cured reinforced polymer composites (hereinafter referred to as "prepregs" were developed in an attempt to overcome some of the disadvantages associated with reinforced polymer materials made according to the lay-up method. Prepregs are used generally for applications in specialist areas such as the aerospace industry.

The term "prepreg" as used herein refers to a partially cured article which comprises a reinforcing web or other such substrate impregnated with a polymeric matrix composition. The composite can be in rod, rope, fibre, roving, strand, tow, sheet or other form. A reinforcing sheet is preferred.

The "prepregging" method has been used in the prior art, for example in the

aerospace industry, to (i) maximise the strength and stiffness of the materials, (ii) minimise the material defects of the materials, and (iii) to create material suitable for temporary storage and easy use. Prepreg materials may also be produced with consistent mechanical properties.

5 The prepregging method involves impregnating fibres (in a uniaxial or multiaxial continuous fabric form) with liquid resin in a manner that controls precisely the fibre-resin volume composition. The liquid resin may be partially cured, so that the resin becomes gel-like (ie: more viscous), but retains its adhesive and reactive properties. The process of partially curing the resin material
10 is known as "B-staging".

Multiple prepregs can then be consolidated into a shaped article.

Accordingly, it is the object of this invention to overcome, or at least alleviate one or more of the difficulties, and/or deficiencies, related to the prior art.

Accordingly, the present invention provides a partially cured reinforced
15 polymeric article which includes:
 a reinforcing web;
 a partially cured cross-linkable polymeric composition, the cross-linkable polymeric composition being formed from:
 an ultra-violet (UV) curable polymeric resin; and
20 a photoinitiator; or
 a photoinitiator and a thermal initiator.

The applicants have surprisingly found that by partially curing the composition in a first stage, a reinforced polymeric article may be prepared very rapidly, e.g. in a matter of seconds. This article may then be stored for an
25 extended period in a suitable manner, and later used and shaped as required, before conducting the final UV and/or thermal cure of the composition.

The reinforcing web may be impregnated with the partially cured cross-linkable polymeric composition.

The partially cured reinforced polymeric article remains in a pliable state so may be folded, or preferably rolled, for ease of storage and transportation, as discussed below.

5 All types of fibre reinforcements or other reinforcing materials commonly used for these applications may be used as the reinforced web. Examples include, but are not limited to, one or more of glass fibres, carbon and graphite fibres, polymeric fibres (including aramide fibres), boron filaments, ceramic fibres, metal fibres, asbestos fibres, beryllium fibres, silica fibres and silicon carbide fibres. Glass fibres, in the form of fibreglass sheets or matts are preferred.

10 The UV curable polymeric resin material may include a curable polyester or vinyl ester resin. An epoxy vinyl ester resin is preferred. A bisphenol-A epoxy resin is particularly preferred. Examples include, but are not limited to, the Nuplex family of resins (polyester resins), and the Derakane family of resins (epoxy vinyl esters) (available from The Dow Chemical Company).

15 As stated above, the partial curing of the polymeric article is achieved by UV radiation.

Any commercially viable UV curing system may be used.

The photoinitiator may be present in any suitable amount to provide the desired level of curing. The amount of initiation may vary depending on the polyester or vinyl ester resin used. Preferably, the photoinitiator is present in an amount from 0.01% to 5% by weight. Most preferably, the photoinitiator is present in an amount from 0.1% to 2% by weight.

25 Examples of photoinitiators which may be used in the present process include, but are not limited to Ciba Geigy Irgacure 819, Ciba Geigy Irgacure 184 (1-hydroxy cyclohexyl phenyl ketone), Ciba Geigy Irgacure 654 (benzildimethyl ketal), Ciba Geigy Irgacure 907 (2-methyl-1-{4-(methylthio)phenyl}-2-morpholino-propanone-1, Merck Darocur 1664, Rohm Catalyst 22, Alcolac Vicure 10 (isobutyl benzoin ether), Alcolac Vicure 30 (isobutyl benzoin ether), and Alcolac Vicure 55

(55) (methyl phenyl glyoxylate phenyl ketone).

Examples of thermal initiators which may be used in the present process include, but are not limited to peroxides including benzoyl peroxide (BPO), cumene hydro peroxide (CHP), 1,1-di-*tert*-butyl peroxy-3,3,5-trimethylcyclo-
 5 hexane, and *sec*-isopropyl percarbonate.

The initiator may include a single component, or a combination of initiator components.

Other additives or modifiers may be present which are conventionally used in resin compositions. Such additives or modifiers may include: inhibitors, UV
 10 stabilisers, UV absorbers, antioxidants, tinting agents, transfer agents, viscosity modifiers, adhesion promoters/modifiers, colourants, fire resistance agents, antistatic agents, fillers, heat stabilisers, thixotropic agents, slip and blocking agents, and air release agents.

Accordingly, a further aspect of the present invention relates to a process
 15 for preparing a partially cured reinforced polymeric article including:

providing

a reinforcing web; and

an effective amount of a cross-linkable polymeric composition
 including:

20 a UV curable polymeric resin and

a photoinitiator; or

a photoinitiator and a thermal catalyst;

impregnating the reinforcing web with the cross-linkable polymeric
 composition and

25 exposing the impregnated web to a source of ultraviolet (UV) radiation for a period and at an intensity sufficient, to partially cure the resin.

The partial UV curing of the resin material may be achieved with exposure of the prepreg to UV light with an intensity of from approximately 1×10^{-5} to 10×10^{-7} W/cm². More preferably, the intensity of the UV light is between 5×10^{-5} and $5 \times$

10^{-6} W/cm².

The partial UV curing of the resin material may be achieved with exposure of the prepreg to UV light for a time sufficient to achieve a desired level of curing. The exposure time is dependent on the light intensity selected but generally will
5 extend from approximately 1 to 120 seconds, more preferably approximately 5 to 60 seconds, most preferably approximately 10 to 45 seconds.

It will be understood that the time of manufacture is accordingly very significantly reduced relative to prior art hand layering methods.

Preferably, the ratio of resin material to fibre material is between
10 approximately 10 and 90% by weight.

More preferably, the ratio of resin material to fibre material is from 25 to 75%, more preferably by 35 to 65% by weight.

Once the prepreps have been partially cured, they are able to be stored. The prepreps may be stored indefinitely for periods up to 1 year when stored in a
15 suitable manner (eg; prevented from exposure to UV light).

As discussed, the partially cured reinforced polymeric article is pliable and may be folded or rolled or otherwise packaged for ease of storage.

As the reinforced polymeric article preferably exhibits a significant degree of tack, one or more surfaces of the article may be provided with a protective layer,
20 both to permit rolling and to avoid contamination with dust and the like during storage.

Accordingly, in a further aspect of the present invention there is provided a laminate polymeric article including
a partially cured reinforced polymeric article as described above; and
25 a first protective coating or film overlaying at least a portion of a surface of the reinforced polymeric article.

The first protective coating or layer may be of any suitable material. A polymeric film or sheet may be used. A thermoplastic polymeric film such as a polyethylene, polypropylene or nylon film is preferred.

5 Where the reinforced polymeric article forms a sheet or film, the protective coating or layer may be applied to one, or preferably both, major surfaces thereof.

In a preferred embodiment of this aspect of the present invention, the partially cured reinforced polymer article may be provided with a protective coating or layer which is UV opaque. This may provide further protection against premature final cure.

10 The UV opaque protective coating may be provided by the first protective layer described above. However, preferably the UV opaque protective coating is a supplementary coating.

Accordingly, in a preferred embodiment, the laminated polymeric article further includes

15 a UV opaque outer coating overlaying at least in part an exposed surface of the partially cured reinforced polymeric article or first protective coating or film.

For example, where the partially cured reinforced polymeric article is provided in a rolled form, the UV opaque outer coating may constitute an outer sheath or sleeve thereover.

20 The UV opaque outer coating may be of any suitable type. A metal material, such as an aluminium foil, may be used. A metal foil is preferred as it is both light and gas impervious and may, in addition, reduce or eliminate loss of volatiles from the partially cured polymeric material.

25 In a further aspect of the present invention, when required to be used, the partially cured polymeric article according to the present invention may be formed into a shaped article. The shaped article may then be subjected to a final curing step. The final cure may be achieved by UV radiation or heat.

Accordingly, in a further aspect of the present invention there is provided a process of forming a shaped article including:

shaping one or more partially cured reinforced polymeric articles (as described above) into a desired form; and

5 subjecting the formed article to a final curing step.

In a preferred form of the present invention, a final cure may include a UV curing step.

Accordingly the process according to this aspect of the present invention may further include exposing the formed article to a source of UV radiation for a
10 period, and at an intensity, sufficient to achieve final cure.

When the resin system is formulated with a photoinitiator only, the final cure may be achieved through further exposure to UV light. The UV light intensity and exposure time is much greater than that used for the partial curing (or B-staging) step.

15 When the complete or final curing of the resin is achieved through a UV cure, the prepregs have a long shelf life, provided they are protected from further incidental UV exposure.

When the resin system is formulated with a photoinitiator and a thermal initiator, the final cure may be achieved at room temperature with exposure to a
20 UV source, or preferably through use of an autoclave or other system which can apply heat and pressure to the composite laminate and provide a more rapid cure.

The intensity and duration of final cure is also dependent on the number of the partially cured reinforced articles (prepregs) utilised in forming the final shaped article. Whilst the relationships are not directly proportional, in general, as the
25 number of layers increases, the intensity and/or duration increases.

The final UV curing of the resin material may be achieved with exposure of the prepreg to UV light with an intensity of from approximately 1×10^{-4} to 1×10^{-6} W/cm². More preferably, the intensity of the UV light is between approximately $5 \times$

10^{-4} and 5×10^{-5} W/cm².

The final UV curing of the resin material may be achieved with exposure of the prepreg a source of UV radiation for a time of from approximately 0.5 to 120 minutes. More preferably, the UV exposure time is from approximately 10 to 45
5 minutes.

In an alternative embodiment, the final curing step may be, or include, a thermal curing.

The process according to this aspect of the present invention includes
subjecting the formed article to a final curing step including applying heat to
10 the shaped article at a temperature and for a period sufficient to achieve a final cure.

Preferably, the temperature of the final cure occurs at a temperature of between approximately 50 and 100°C. More preferably, the temperature is between approximately 65 and 80°C.

15 Preferably, the pressure applied during the final cure is between approximately 30 and 100 psi. More preferably, the pressure is between 50 and 70 psi.

In a further aspect of the present invention there is provided a cured shaped article formed as described above.

20 The present invention will now be more fully described with reference to the accompanying examples. The examples describe UV B-staging for a number of systems with different fibre and resin combinations, and for two different UV B-staging processes.

It should be understood that the description following is illustrative only and
25 should not be taken in any way as a restriction on the generality of the invention described above.

EXAMPLES

General

The tack for each prepreg was measured using a floating roller peel test based on ASTM D3167. The average force to peel the prepreg from a rigid aluminium substrate is used as the measure of tack. Increasing tack force is consistent with an increase in resin mass fraction.

EXAMPLE 1

Glass/polyester prepreg for UV B-staging and UV final cure

A polyester resin (Nuplex F61042) was formulated with 0.5 parts per hundred of Irgacure 819 photoinitiator. A quadraxial glass-fibre fibre fabric (1200 gsm) and a Twill glass-fibre fibre fabric (385 gsm) was impregnated with the liquid resin then passed under a 400 watt Mercury vapour lamp. The UV light intensity was 7×10^{-7} W/cm² and the exposure time ranged from 15 to 30 seconds.

The resin mass fraction was 35% in the Quadraxial prepreg and 50% in the Twill prepreg. The shelf life of these products is at least 6 months when protected from UV exposure. The final cure is achieved through further UV exposure of greater intensity and/or time.

EXAMPLE 2

Glass/polyester prepreg for UV B-staging and UV final cure:

A polyester resin (Nuplex F61042) was formulated with 0.5 parts per hundred of Irgacure 819 photoinitiator. A woven roving glass-fibre fibre fabric (635 gsm) was impregnated with the liquid resin. B-staging was done under a UVA blacklight using 2x20 watt tubes. The UV intensity in the UVA range was approximately 4.7 mW/cm² and the exposure time was 10 seconds.

The resin mass fraction was 50%. The shelf life of this product is at least 6 months when protected from UV exposure. The final cure is achieved through

further UV exposure of greater intensity and/or time.

EXAMPLE 3

Glass/vinylester prepreg for UV B-staging and UV final cure:

5 A vinylester resin (Dow Derakane 411-350) was formulated with 0.5 parts per hundred of Irgacure 819 photoinitiator. A quadraxial glass-fibre fibre fabric (1200 gsm) was impregnated with the liquid resin in a 1:1 mass ratio, and then passed under UVA blacklight. The UV light intensity in the UVA range was approximately 4.7 mW/cm² and the exposure time was 10 seconds.

10 The resin mass fraction was 50%. The shelf life of this product is at least 6 months when protected from UV exposure. The final cure is achieved through further UV exposure of greater intensity and/or time.

EXAMPLE 4

Glass/polyester prepreg for UV B-staging and final thermal cure:

15 A polyester resin (Nuplex F61042) was formulated with 0.5 parts per hundred (pph) of Irgacure 819 photoinitiator, and 4 pph benzoyl peroxide (BPO) or 1 pph cumene hydro peroxide (CHP) thermal catalysts. A quadraxial glass-fibre fibre fabric (1200 gsm) was impregnated with the liquid resin in a 1:1 mass ratio, and then passed under UVA blacklight. The UV light intensity in the UVA range was approximately 4.7 mW/cm² and the exposure time was 10 seconds.

20 The shelf life of this product at room temperature is limited due to the presence of the thermal catalyst in the resin formulation. It must also be protected from UV exposure when stored. Final cure can be achieved through further UV exposure but this is example is specifically for manufacturers who prefer a thermal cure prepreg. The formulation with BPO will require 80°C for 15-20 minutes. The
25 formulation with CHP will require 100°C for 10-15 minutes.

EXAMPLE 5***Glass/vinylester prepreg for UV B-staging and final thermal cure:***

A vinylester resin (Dow Derakane 411-350) was formulated with 0.5 parts per hundred of Irgacure 819 photoinitiator, and 4 pph benzoyl peroxide (BPO) thermal catalyst. A quadraxial glass-fibre fibre fabric (1200 gsm) was impregnated with the liquid resin in a 1:1 mass ratio, and then passed under UVA blacklight. The UV light intensity in the UVA range was approximately 4.7 mW/cm² and the exposure time was 10 seconds.

The shelf life of this product at room temperature is limited due to the presence of the thermal catalyst in the resin formulation. It must also be protected from UV exposure when stored. Final cure can be achieved through further UV exposure but this is example is specifically for manufacturers who prefer a thermal cure prepreg. With BPO in the formulation, a thermal cure of 80°C for approximately 20 minutes is required.

It will be understood that the invention disclosed and defined in this specification extends to all alternative combinations of two or more of the individual features mentioned or evident from the text or drawings. All of these different combinations constitute various alternative aspects of the present invention.

It will also be understood that the term "comprises" (or its grammatical variants) as used in this specification is equivalent to the term "includes" and should not be taken as excluding the presence of other elements or features.

Australian Composites Pty Ltd

By its Registered Patent Attorneys

Freehills Carter Smith Beadle

4 December 2002

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